SYNTHESIS AND CONVERSION STUDIES OF POLYMERIC MODELS FOR LOW-RANK COALS

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INTRODUCTION

Efforts to understand the key chemical reactions responsible for coal conversion have been severely hindered over the years by the necessity of having to infer a complex sequence of chemical reactions for a substrate, coal, whose critical linkages are basically unknown. To aid in the effort, many workers have studied the reactions of coal "models" under various conversion conditions. However, this already imperfect solution has itself been limited by the inappropriateness of many of the models, and by the widespread misconception that the spontaneous thermal scission of inherently weak linkages in the coal structures is solely responsible for the fragmentation of the coal matrix. In fact, the combination of these two factors has compounded the situation: the perception of control by homolysis of weak linkages has led to a disporportionate focus on weakly bonded models such as bibenzyl, benzylphenyl ether, and related structures. This paper reports the initial results of an effort to use model structures that (1) have inter-cluster linkages that are perhaps more representative of those in coals, and (2) are incorporated into polymeric networks in order that mass transport and other effects that can be important in heterogeneous systems might be more appropriately mimicked.

The basic linkage chosen for the present study is the oxy-ethylene linkage of phenyl phenethyl ether. Although phenyl phenethyl ether and related structures have been previously studied as coal models (1-4), they have not received the attention commensurate with their recognized abundance in lignins. No studies, to our knowledge, have been reported for specially synthesized and characterized polymers containing this linkage. As it happens, the weakest bond in phenyl phenethyl ether, the phenoxy-carbon bond, is about equal in strength to the central bond in bibenzyl (5,6). At ~61 kcal/mol, the bibenzyl bond is undergoes homolysis at 400°C with a half life of ~25 hours, but as has been well-demonstrated in studies of several three-atom-linked di-aryls (1-4), homolysis typically serves only as the initiation process for their decomposition. In the case of phenyl phenethyl ether itself, the very facile β-scission of the benzylic radical formed by H-abstraction results in an observed half-life (at 400°C) that is at least 10 times shorter than that for the homolysis (2). Clearly, either coals do not have very many such linkages, or some other factor (viz., retrograde reaction) counteracts the demonstrated reactivity of the -O-C-C- linkage. Interestingly, low-rank coals have for a long time been known to be more reactive than bituminous coals, but they give lower liquefaction conversions. Therefore, it seems likely that a crosslinked or intertwined polymeric network, or the presence of additional functional groups (i.e., -OH, -OMe, or -COOH) result in a proclivity for retrograde reactions that makes coals with very labile linkages unusually hard to convert. To better understand those retrograde processes and the approaches that might be used to limit them, we have embarked on a program to synthesize, characterize, and study the conversion of the polymeric, three-atom-bridged models described below.

RESULTS

Polymer Synthesis

We prepared two three-atom-bridged polymers of the -O-C-C- type, and for a baseline comparison, the corresponding -C-C-C- type polymers. This paper focuses on the synthesis, characterization, and initial conversion studies of two variations of the -O-C-C- linked polymers.
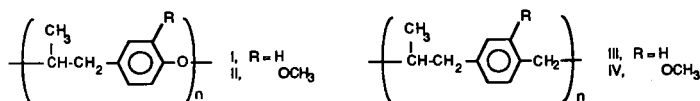

Polymers containing the -O-C-C- linkage between single phenyl rings have been prepared by the oxymercuration of eugenol ($R = OCH_3$) and 4-allylphenol ($R = H$). Eugenol was obtained from Aldrich Chemical, Inc. 4-Allylphenol was obtained by custom synthesis from Saber Laboratories (Morton Grove, Illinois). The polymerization was conducted at 80°C in nitromethane solvent using dry $Hg(CF_3CO_2)_2$ as a catalyst. The low nucleophilicity of the trifluoroacetate (TFA) allows for attack on the mercurated complex by the phenolic oxygen resulting in polymerization of the substrate. Mercury was removed from the intital polymerization product using sodium borohydride.
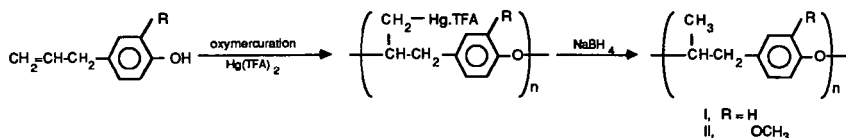
The polymers were characterized using elemental analysis, GPC, NMR, and field ionization mass spectrometry (FIMS). GPC shows that the poly(eugenol) sample discussed here has a broad distribution of molecular weights (1×10^4 to 2×10^6; $M_n \sim 2 \times 10^5$). The poly(p-allyphenol) sample, on the other hand, has a narrow MW range with a $M_n \sim 5 \times 10^6$. Light scattering experiments confirmed the very high molecular weights of these polymers. The polymers are insoluble in most common solvents and only sparingly soluble in cold DMF. However, they have high solubility in hot DMF. ^{1}H NMR peak area ratios were generally consistent with the expected ratios, but were not highly precise, owing to limited solubility in the cold DMF as well as interference from water and traces of protonated solvent in the deuterated DMF. ^{13}C CPMAS NMR of the solid samples is also consistent with the expected structure, however, reliable quantitative information on the relative amounts of alkyl and aryl protons could not be obtained. Improved solution phase NMR will be obtained with new, lower molecular weight samples that are currently being prepared. Elemental analysis (Galbraith Laboratories) in both cases indicates H/C ratios slightly lower than expected (0.99 and 0.97 vs calculated values of 1.20 and 1.11 for the poly(eugenol) and poly(4-allylphenol), respectively).

Initial efforts to produce well-characterized -C-C-C- polymers have used the following reaction sequence:


431
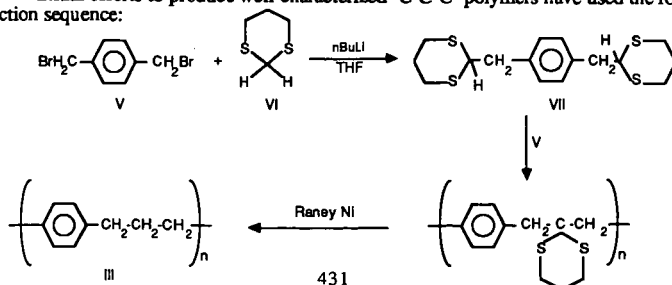
The α,α'-dibromo-p-xylene (V) was treated with the monoanion of dithiane (VI) in THF at -50° to -30°C. The product (VII) was characterized by TLC and NMR and found to consistent with the anticipated structure. The dianion from VII was treated with the dibromide (V) at low temperatures for 3 hours and thereafter at room tempeature for 15 hours. The THF-soluble fraction showed a polymer of MW ~2500. Desulfurizarion of the THF-soluble portion was effected using Raney Ni and the product was exhaustively extracted to yield a polymer of MW ~1500. Elemental analysis gave C= 83.86% and H = 8.7%, indicating an H/C ratio of 1.24 (as compared with an expected ratio of 1.11).

Polymer Characterization by Pyrolysis-FIMS

As with the elemental and NMR analyses, the Py-FIMS characterization of the poly(eugenol) and the poly(4-allylphenol) is appropriatedly described as consistent with, but not conclusive evidence of, the desired structures. Since the FIMS characterization of a material that is not volatile under high-vacuum conditions involves programmed-temperature heating to pyrolytically generated volatiles that are then mass spectrometrically analyzed, it constitutes a thermal conversion experiment that bears relevence to coal liquefaction or pyrolysis. Therefore the Py-FIMS results will be discussed in some detail.

The Py-FIMS spectra of the poly(eugenol) and the poly(4-allylphenol) are shown in Figures 1 and 2. The spectra are relatively simple and are dominated by C_1- to C_3- phenols or dihydroxybenzenes (catechols), and, in the case of the poly(eugenol), by an ion corresponding to the monomer (m/z 164). These products are all to be expected from the desired polymer structure. However, the relative amounts of the various fragments are quite unexpected, indicating either that the decomposition sequence is not as anticipated, or the polymer structure is not exactly as desired, or both.

In both cases, the sequence of oligomeric groupings commonly seen in Py-FIMS of linear polymers (7) is essentially absent. The poly(eugenol) (Figure 1) has a large peak at m/z 164, representing the monomer, but very little intensity in the vicinity of the dimer (m/z 328), and none in the vicinity of the trimer (m/z 492) The spectrum of the poly(4-allylphenol) is even more pronounced in this regard: there is only moderate intensity at the monomer (m/z 134) and essentially none at the dimer and trimer masses (268, 402). The ten-fold decline in intensity of the dimer relative to the monomer, and the total absence of any ion intensity corresponding to the trimer is highly unexpected for a linear polymer that cannot unzip and is thus limited to scission by random attack on its linkages. The principal expected bond scission pathways shown below for the case of the eugenol polymer should occur randomly along the polymer chain and would result in a whole sequence of oligomers, as has been reported in the pyrolysis of other linear polymers.(7)

Isoeugenol   Scheme 1
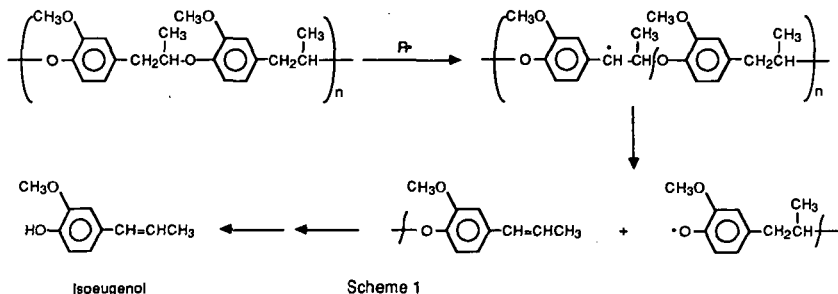
Along with the absence of higher oligomers, Figures 1 and 2 also show that each polymer yields substantial amounts of several alkylated dihydroxybenzenes and phenols, respectively. In the case of poly(eugenol), the C_1- and C_2- dihydroxybenzenes are of comparable abundance to the monomer itself. In the case of the poly(4-allylphenol), C_1- and C_2- phenols are about ten times as abundant as the monomer. In both cases, the sum of C_1- , C_2- and C_3- phenols is substantially greater than the intensities of the monomers themselves.

Examination of the temperature dependence for evolution of the major peaks in Figures 1 and 2 suggests there are separate production routes for the monomers and the more highly fragmented phenolics, at least in the case of the poly(eugenol). Figures 3 and 4 show the abundance of the individual peaks as a function of temperature for the two polymers. In the case of poly(4-allylphenol) (Figure 3), the monomer and the C_1- phenol evolve at similar temperatures. On the other hand, in the case of poly(eugenol) (Figure 4), there is substantial evolution of the monomer (164) well below 300°C, while the methyl catechol (124) does not peak until about 400°C.

Preferred evolution of the monomers at lower temperatures is consistent with the expectation (1-3,8) that depolymerization results from H-abstraction--β-scission chain processes, as depicted above in Scheme 1. The C_1- to C_3- phenols and catechols, on the other hand, do not have easily identifiable chain routes, and would be expected to be rapidly evolved only at higher temperatures. Monomer evolution is expected to be more facile for poly(eugenol) because the methoxy group decreases the strength of the phenoxy-carbon bond in the -O-C-C- linkage by about 4 kcal/mol (9, 10). All other things being equal, this decrease in bond strength would be expected to decrease by about 150°C the temperature at which an equivalent decompostion rate is observed. As Figures 3 and 4 show, the peak of monomer evolution in poly(eugenol) is at least 150°C lower than for poly(4-allylphenol). This result may have bearing on the as-yet unresolved question (8) of whether phenyl phenethyl ether-type structures are a class for which concerted decomposition in a retro-ene process is competitive with the free radical chain process shown above (Scheme 1).

The mode of formation of the C_1- to C_3- catechols and phenols is even more puzzling than the oligomer distribution. Possible routes to the C_1- to C_3- catechols could involve initial methyl-phenoxy cleavage, as the homolysis of the ca. 61 kcal/mol methyl-O bonds becomes rapid in the vicinity of 400°C. However, this suggestion is not consistent the fact that the yield of C_1- and C_2- phenolics, is actually greater for the poly(4-allylphenol), which has no methoxy group, nor with the fact that the evolution of methylphenolics reaches its maximum at about the same temperature for both the poly(eugenol) and the poly(4-allylphenol).

Liquefaction of -O-C-C- Polymers

The batch microautoclave liquefaction results for poly(eugenol) and poly(p-allylphenol), and for comparison, the results for a weakly linked (-O-C-) polymer and a sample of the Argonne Zap Lignite are shown below.

PRODUCT YIELDS[a] IN THE LIQUEFACTION OF MODEL POLYMERS

Sample	Hexane-Solubles	Toluene-Solubles	Pyridine-Solubles	Toluene-Insolubles	Pyridine-Insolubles	Gas
Poly(eugenol)	27	66	93	27	0	8
Poly(4-allylphenol)	1	52	96	44	0	5
Polymer VIII	85	96	100	4	0	3
Zap Lignite	14	28	46	62	50	5

[a] The liquefaction tests were performed in a microautoclave reactor, using 9,10-dihydrophenanthrene as the solvent. The reactor was purged and sealed under N_2, and then immersed in a sand bath at 400°C for 30 minutes.
[b] Polymer VIII is a linear polymer having the structure:
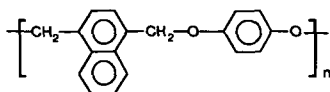
The hexane- and toluene-soluble conversions of the two -O-C-C- linked polymers are in the same order as the Py-FIMS volatilities (53 and 28%, respectively for the poly(eugenol) and the poly(4-allylphenol). They are substantially harder to convert than the weakly bonded Polymer VIII, but, in the case of the poly(eugenol), easier to convert than low-rank coal. The similarities and differences will be further considered in the Discussion Section.

DISCUSSION

The fact that the pyrolysis products are dominated by lower oligomers and smaller fragments does not, by itself, indicate whether the crosslinks were pre-existing or were generated in the course of the thermal treatment. This question is of course central to both the characterization of the original polymers, and also to an understanding of their behavior under liquefaction and other conversion conditions. Comparison of the conversion of the two -O-C-C-linked polymers with the "conversion" of other three-atom-linked models, including phenyl phenethyl ether itself, shows the apparent rate of polymer conversion to be somewhat slower than expected. Gilbert and Gajewski report (2) apparent rate parameters for phenyl phenethyl ether decomposition that correspond to a half-life at 400°C of about two hours . Considering that the linkages are somewhat weaker in both poly(4-allylphenol) and poly(eugenol) (5,9), and that many fewer than half the linkages need to be broken to make either of these polymers, if linear, fully soluble in toluene certainly supports the other indications of significant crosslinking at some stage. We are presently preparing additional batches of the poly(4-allylphenol) with phenol added during the synthesis to purposely terminate the growing polymer chains at a molecular weight level well below one million.

In general, the behavior of these two polymers is similar to the behavior of other polymeric models that are either crosslinked to begin with or are easily crosslinked during conversion and to the behavior of low-rank coals themselves, as previously discussed by Solomon and coworkers (7, 11-13). A high degree of crosslinking results in cleavage to free, and hence volatile, fragments of mainly small units, rather than large segments of a linear polymer chain. In addition, the high yields of the dihydroxybenzenes and the cresols are specifically quite similar to products generated during the pyrolysis (or liquefaction) of lignites and subbituminous coals (11-13).

Specifically, the poly(eugenol): (1) has a linkage known to be highly reactive; (2) begins to produce some monomer at temperatures lower than 200°C; (3) is nevertheless rather hard to fully convert to soluble or volatile products; and (4) has as its most abundant pyrolysis products those same alkylated catechols that tend to dominate the pyrolysis products of lignites and subbituminous coals. In other words, it bears a rather curious similarity to low-rank coals, given the limited range of structures in the original polymer. Thus it appears that these polymeric models containing -O-C-C- linkages may represent appropriate structures for use in determining the chemical details (and therefore what controls) the facile retrograde reactions of low-rank coals.

ACKNOWLEDGEMENTS

REFERENCES

1.   Poutsma, M. L.; Dyer, C. W., *J. Org. Chem.*, **1982**, *47*, 4903.

2.   Gilbert, K. E.; Gajewski, J. J., *J. Org. Chem.*, **1982**, *47*, 4899.

3.   Gilbert, K. E., *J. Org. Chem.*, **1984**, *49*, 6.

4. Klein, M. T.; Virk, P. S., *Ind. Eng. Chem., Fundam.*, **1983**, 22, 35.

5. McMillen, D. F.; Golden, D. M. "Hydrocarbon Bond Dissociation Energies," *Annu. Rev. Phys. Chem.*, **1982**, *33*, 497.

6. Pedley, J. B.; Naylor, R. D.; Kirby, S. P., *Thermochemical Data of Organic Compounds*, 2nd Ed., Chapman and Hall, New York, 1986.

7. Squire, K. C.; Solomon, P. R.; Carangelo. R. M.; DiTaranto, M. B., Fuel, **1986**, *65*, 833.

8. Poutma, M. L., "A Review of Thermolysis Studies of Model Compounds Relevant to Processing of Coal," Report ORNL.TM-10637, Oak Ridge National Laboratory, 1987.

9. Suryan, M. M.; Kafafi, S. A.; Stein, S. E., *J. Am. Chem. Soc.*, **1989**, *111*, 1423.

10. Benson, S.W., *Thermochemical Kinetics*, 2nd ed., John Wiley and Sons, Inc., New York, 1976.

11. Serio, M. A.; Solomon, P.R.; Carangelo, R. M., *Am. Chem. Soc. Div. Fuel Chem. Preprints,* **1988,** *33(2)*, 295.

12. Deshpande, G. V.; Serio, M. A.; Solomon, P.R., *Am. Chem. Soc. Div. Fuel Chem. Preprints,* **1988,** *33(2)*, 310.

13. Solomon, P. R.; Serio, M. A.; Deshpande, G. V.; Kroo, E., "Crosslinking Reactions during Coal Conversion" accepted for publication in *Energy & Fuels,* **1990**.
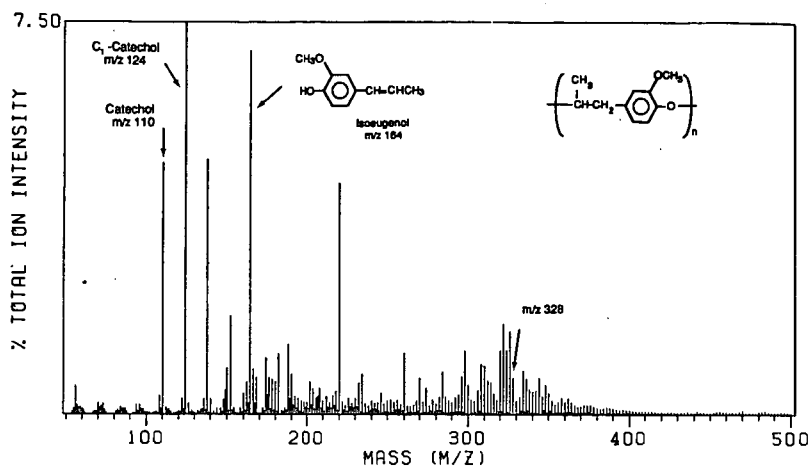
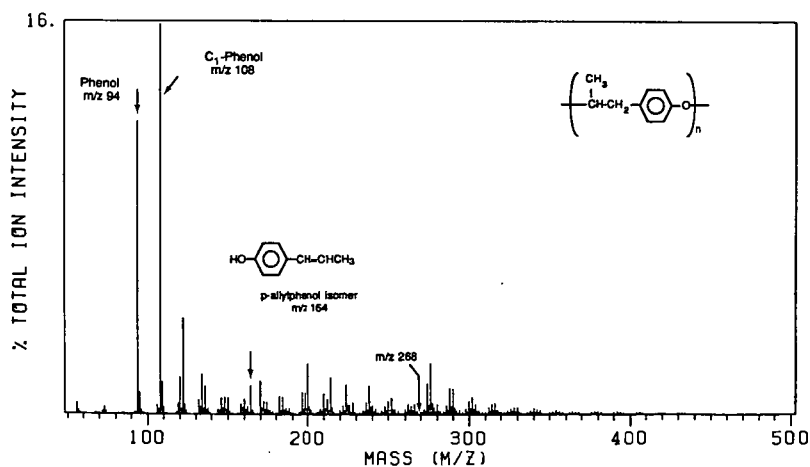Figure 1. Pyrolysis-FI mass spectrum of poly(eugenol).

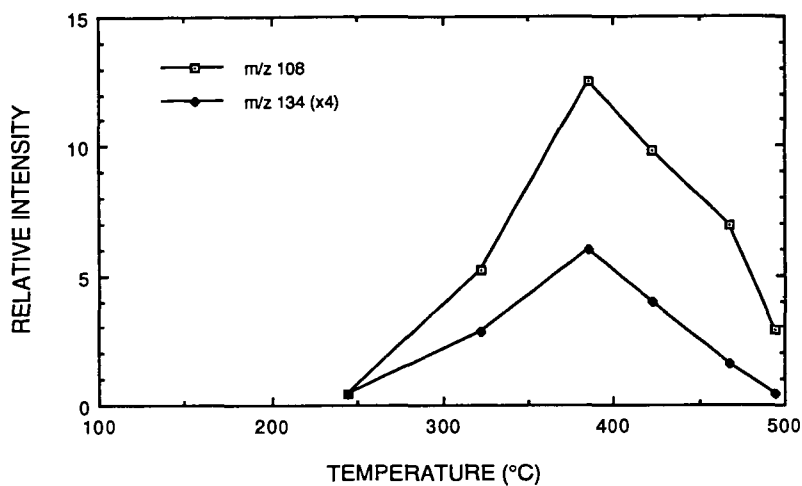Figure 2. Pyrolysis-FI mass spectrum of poly(p-allylphenol).

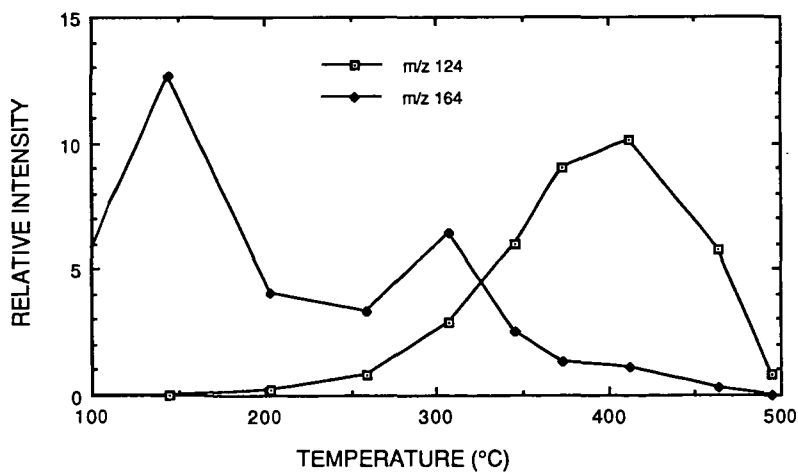Figure 3. Thermal evolution of cresol and monomer from poly(4-allylphenol).

Figure 4. Thermal evolution of methyl dihydroxybenzene and monomer from poly(eugenol).